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1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
26-09-2008	Final Performance	1 Dec. 2003 – 31 May 2008

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Molecular Dynamics Simulation of Supercritical Spray Phenomena	
	5b. GRANT NUMBER FA9550-04-1-0012
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
Michael M. Micci	
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
The Pennsylvania State University Department of Aerospace Engineering 229 Hammond Building University Park, PA 16802	

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
Air Force Office of Scientific Research 875 North Randolph Road Suite 325, Room 3112 Arlington, VA 22203	AFOSR/NA
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-SR-AR-TR-08-0510

12. DISTRIBUTION / AVAILABILITY STATEMENT

Distribution A: Approved for Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Results showed that the way the fluid-wall interaction is modeled in molecular dynamics simulations has a strong effect on the resultant simulation of liquid injection into a gas. It was found that modeling the wall as individual atoms (atomistic model) interacting with the fluid resulted in the fluid remaining in an injection tube absent any pressure or body force to force it into a gaseous region while a stochastically modeled diffusely reflecting wall with no attraction between the fluid and the wall resulted in the fluid being injected into the gas even in the absence of pressure or body forces. Since a non-atomistically modeled wall has reduced computational requirements compared to an atomistic wall, efforts centered on an examination of possible non-atomistic continuous fluid-wall interaction models that would not only correctly reproduce fluid thermodynamic properties such as pressure but would also reproduce the same fluid injection behavior as an atomistic wall model. Several non-atomistic fluid-wall models were examined in terms of their ability to correctly predict the fluid pressure in the injection tube over a range of fluid densities as well as their ability to reproduce atomistic wall injection behavior, but none were found able to reproduce atomistic wall behavior.

15. SUBJECT TERMS

Molecular dynamics, supercritical, sprays, liquid rockets

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
Unclassified			None	9	Mitat Birkan
a. REPORT X	**b. ABSTRACT** X	**c. THIS PAGE** X			**19b. TELEPHONE NUMBER** *(include area code)* 703-696-7234

Molecular Dynamics Simulation of Supercritical Spray Phenomena

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FA9550-04-1-0012

Final Performance Report for the Period

12/1/2003 – 5/31/2008

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Abstract

Results showed that the way the fluid-wall interaction is modeled in molecular dynamics simulations has a strong effect on the resultant simulation of liquid injection into a gas. It was found that modeling the wall as individual atoms (atomistic model) interacting with the fluid resulted in the fluid remaining in an injection tube absent any pressure or body force to force it into a gaseous region while a stochastically modeled diffusely reflecting wall with no attraction between the fluid and the wall resulted in the fluid being injected into the gas even in the absence of pressure or body forces. Since a non-atomistically modeled wall has reduced computational requirements compared to an atomistic wall, efforts centered on an examination of possible non-atomistic continuous fluid-wall interaction models that would not only correctly reproduce fluid thermodynamic properties such as pressure but would also reproduce the same fluid injection behavior as an atomistic wall model. Several non-atomistic fluid-wall models were examined in terms of their ability to correctly predict the fluid pressure in the injection tube over a range of fluid densities as well as their ability to reproduce atomistic wall injection behavior, but none were found able to reproduce atomistic wall behavior.

Accomplishments/New Findings

In molecular dynamics (MD) simulations, the solid boundary conditions are modeled in two ways:

Atomistic wall model: the wall has a molecular structure included in the modeled system.

Continuous solid boundary model: the wall structure is modeled through a mathematical or a functional model. In the mathematical model, the wall model acts as an impulsive force acting on the fluid particle only when it crosses the imposed boundary, an example being a diffusely reflecting wall as is used in rarefied gas dynamics. The functional wall model corresponds to a force that acts on the fluid particles but within a range of interaction and not only at the boundary.

Atomistic wall models are usually used if the main physical property studied is the fluid/solid interactions. The clear disadvantage of the atomistic model is its computational cost. The attraction of the functional model versus the mathematical model is the 'longer' range of interaction that might limit the fluid slip values at the boundary. However, no attempt to compare these models is available in the literature. No work to assess the consequences these models would have on especially dense phases and to determine which criteria has a predominant effect in order to choose one or the other model has been published.

Pressure calculations are used to initially assess wall models differences since it is closely related to the fluid structure observed in a bounded medium at the nanoscale. Pressure is computed using the virial formula

$$P = \frac{N}{V} k_B T - \frac{1}{6V} \left\langle \sum_i \sum_{j \neq i} \frac{\partial \phi(r_{ij})}{\partial r_{ij}} \cdot r_{ij} \right\rangle \tag{1}$$

where $\square$ is the interatomic potential between two atoms i and j and r_{ij} is their separation distance.

Pressure was first calculated for liquid argon confined by an atomistic wall, which is supposed to be the closest wall model to reality, especially at the nanoscale[1]. Figure 1 shows that the calculated pressure matches the experimentally measured pressure over a wide range of liquid densities. The atomistic wall also gives a fluid density that is slightly lower in the center of the bounded region than the mean density due to the attractive (wetting) forces between the wall and fluid atoms.
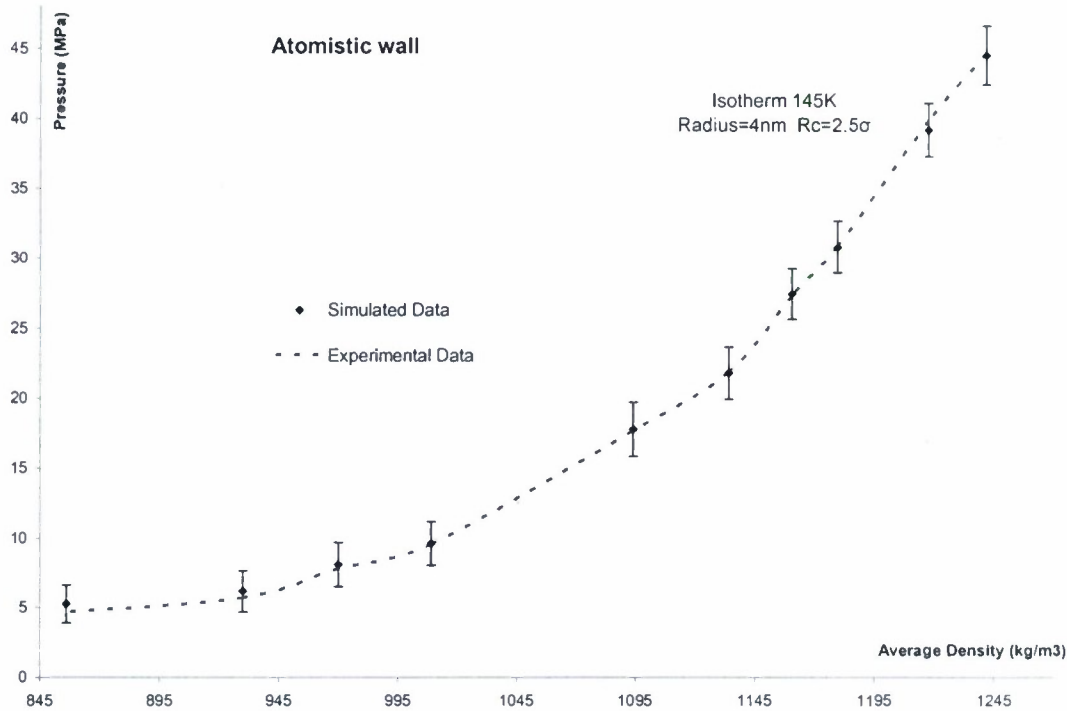

Fig.1   Calculated and measured pressures for liquid argon confined by an atomistic wall.

Pressures were then calculated for several continuous wall models.   The diffusely reflecting stochastic wall model, like the atomistic wall, was able to reproduce experimentally measured pressures over the density range of interest as shown in Figure 2.
However, it produced a center density higher than the mean density, contrary to what is observed experimentally on the atomistic level[2].
The wetting property of a those two models is shown in Figure 3. It is interesting to see that the growth of the 'solid-like' layer near the boundaries is linear in both cases. The slope of the average density to the channel center density is controlled by the strength of the solid-fluid interaction. This slope is lower than unity for a wetting wall and higher in the case of a purely diffuse wall.

[1] Yi, P., Poulikakos, D., Walther, J. and Yadigaroglu, G., "Molecular Dynamics Simulation of Vaporization of Ultra Thin Liquid Argon on a Surface," *Int. J. of Heat and Mass Transfer*, Vol. 45, No. 10, 2002, pp. 2087-2100.
[2] Israelachvili, J. N., *Intermolecular and Surface Forces*, 1992, Academic Press, New York.
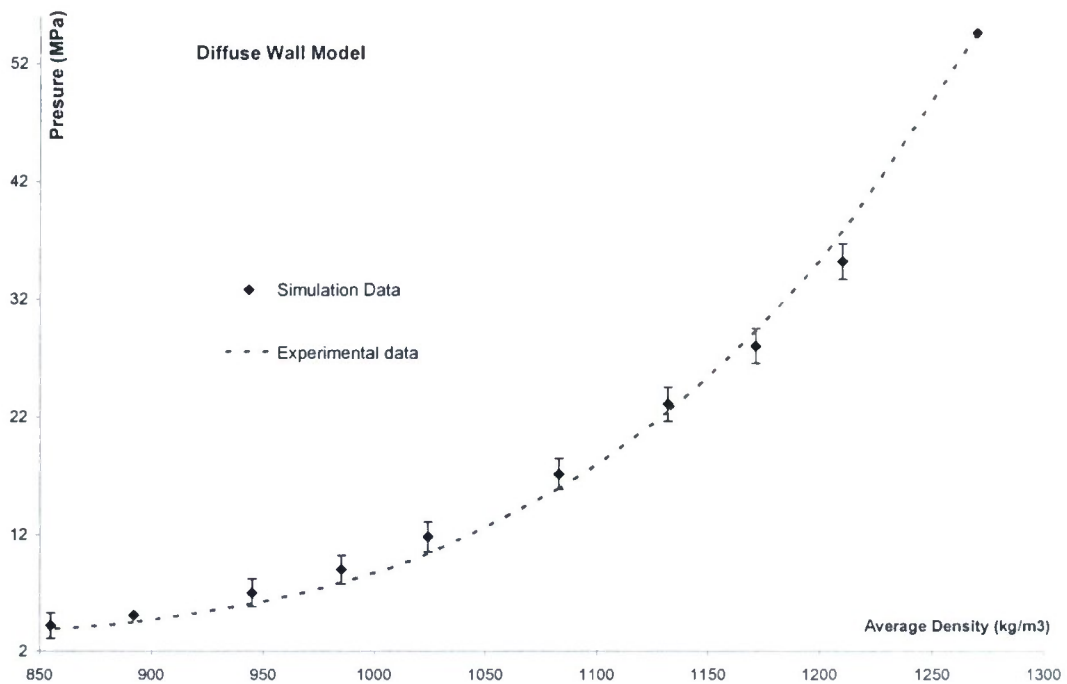
Fig.2   Calculated and measured pressures for liquid argon confined by a diffuse wall.
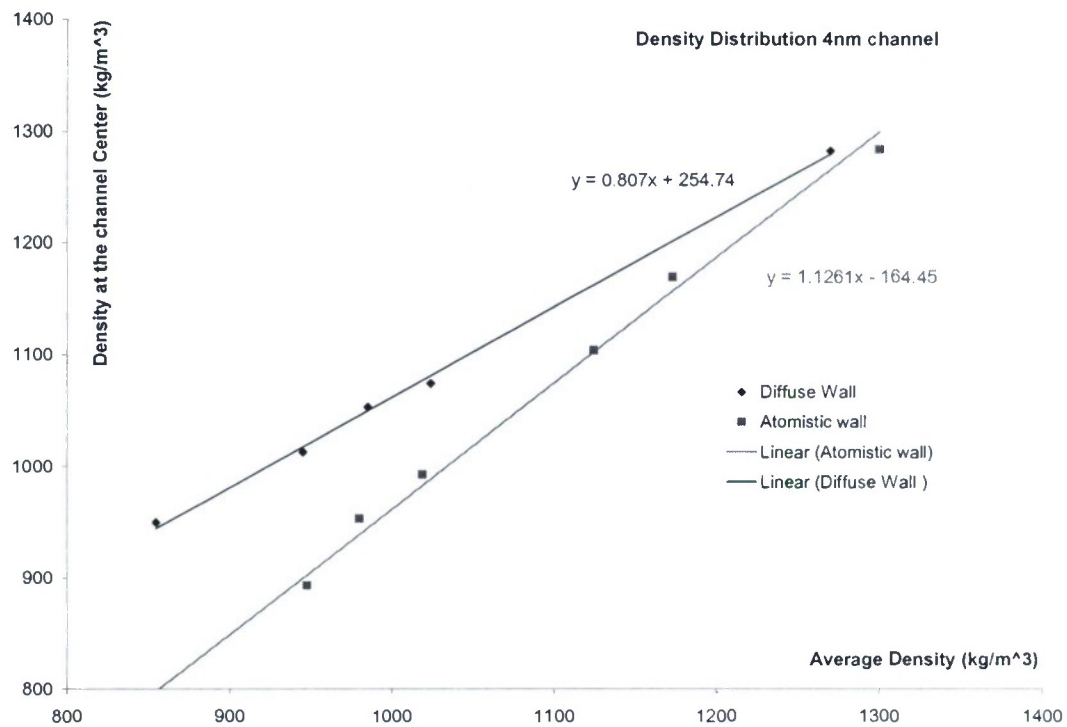

Fig.3   Wall Wetting property: atomistic vs. diffuse wall models.

The first functional wall model examined was a Morse potential combined with a diffusely reflecting boundary to add an attractive force between the wall and the fluid[3]. The Morse potential is given by

$$U_w = \varepsilon_{wf}\left[\exp\left(-2\alpha R_{sep}\right) - 2\exp\left(-\alpha R_{sep}\right)\right] \qquad (2)$$

where R_{sep} corresponds to the normal distance of the particle to the wall and the inverse of α provides the range of interactions. In order to remove the impulsive force, a combination of two Morse potentials with different parameters to create both repulsive and attractive forces was tried. Unfortunately, the velocity rescaling and reversing at the boundary is still needed since the repulsion portion goes to zero at the surface, allowing some particles to cross the wall. As shown by Figure 4 below, the combined Morse potential model best matches measured pressures across the density range. The density in the center of the system was lower than the mean density in accord with experimental data if the Morse potential was strong enough (otherwise the diffuse wall behavior is dominant).
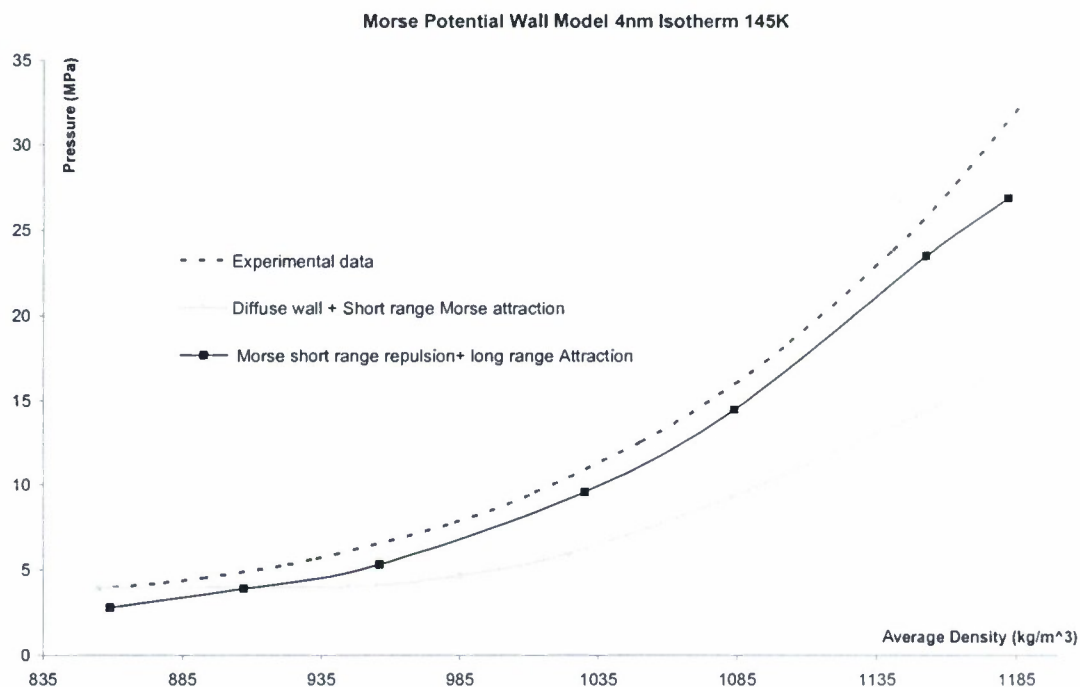
Morse Potential Wall Model 4nm Isotherm 145K

Fig. 4 Calculated pressure using single and combined Morse potential wall models compared to measured pressures as a function of density.

The second functional wall model to be examined was a continuous Lennard-Jones 10-4 potential[4,5]. The form of the wall potential is:

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[3] Castillo-Tejas, J., Alvarado, J. F. J., Gonzalez-Alatorre, G., Luna-Barcenas, G. and Sanchez, I. C., "Nonequilibrium Molecular Dynamics of the Rheological and Structural Properties of Linear and Branched Molecules. Simple Shear and Poiseuille Flows; Instabilities and Slip," *J. Chem. Phys.*, Vol. 123, 2005, p. 054907.

[4] Abraham, F., "The Interfacial Density Profile of a Lennard-Jones Fluid in Contact with a (100) Lennard-Jones Wall and its Relationship to Idealized Fluid/Wall Systems: A Monte Carlo Simulation," *J. Chem. Phys.*, Vol. 68, No. 8, 1978, pp. 3713-3716.

[5] Steele, W. A., *The Interaction of Gases with Solid Surfaces*, 1974, Pergamon Press, New York.

$$U_w(R_{sep}) = 2\pi n \varepsilon_{wf} \sum_{i=1,2} \left(\frac{2}{5} \frac{\sigma_{wf}^{12}}{R_{sep_i}^{10}} - \beta \frac{\sigma_{wf}^{6}}{R_{sep_i}^{4}} \right) \tag{3}$$

where n is the surface density, R_{sep} is the separation distance between a fluid particle and a given layer of the wall (either one or two layers) along the normal direction and β is a parameter added to control the attraction by comparison to the repulsion. This form of the potential (10-4) is a surface integration of the Lennard-Jones 12-6 potential over one layer of solid atoms. The corresponding theoretical integration over the total volume of the atomistic wall is of the form of a Lennard Jones (9-3).

However, a numerical summation of the wall-fluid potentials for our configuration of the atomistic wall, averaged over the fluid particles, results in a Lennard-Jones 6-3 potential as illustrated in Figure 5.
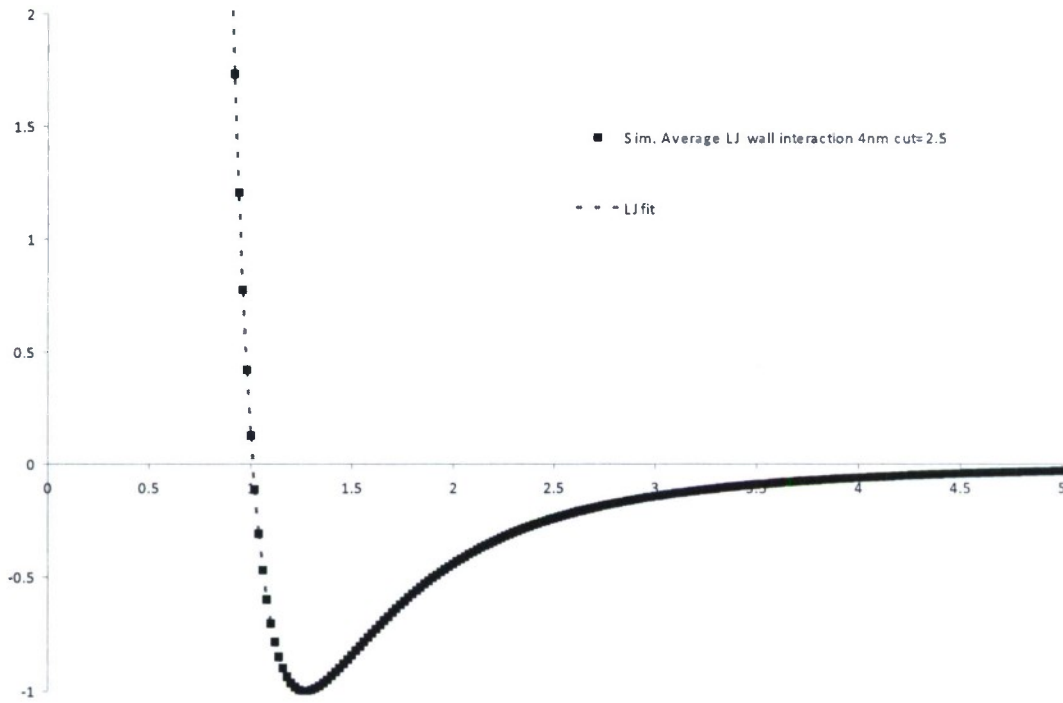

Fig. 5 Calculated average potential for an atomistic wall and LJ6-3 Fit.

Figure 6 show that all the Lennard Jones wall models provide a good agreement between the simulated pressure and the expected data for a wide range of liquid densities if the wall parameters are well chosen. Discrepancies appear mostly at very high density. They also provide lower densities in the channel center by comparison to the average density which secures the wetting property for the given wall model.
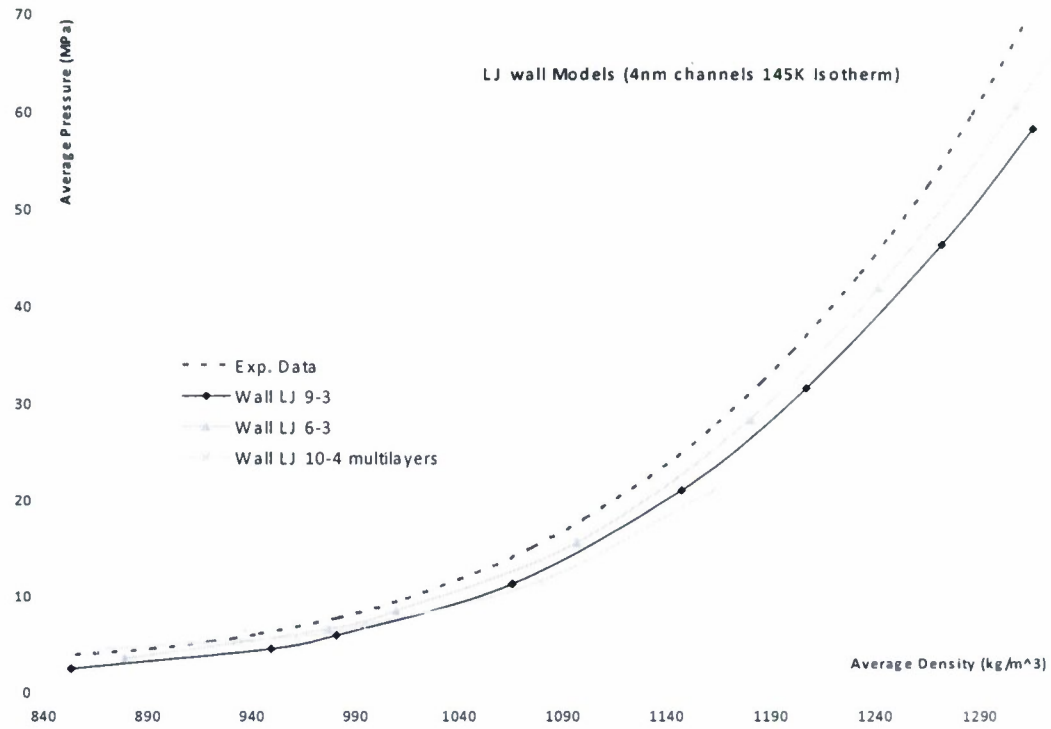
Fig. 6 Calculated pressure for different Lennard-Jones functional wall models.

Simulations of the behavior of liquid in a confined cylinder adjacent to a larger gaseous region in the absence of any pressure or body force acting on the fluid were conducted for the seven wall models: atomistic, diffusely reflecting stochastic, combined Morse plus diffusely reflecting, and Lennard-Jones 10-4, 9-3 and 6-3. Illustration of the injection process at time $0.3\mu s$ for all wall models is shown in Figure 7. It is found that Morse plus diffusely reflecting wall model produced results that most closely matched the atomistic wall model injection behavior where 'melting' of the interface liquid/gas occurs. However, as shown in Figure 2 above, the Morse plus diffusely reflecting wall model does not accurately predict the fluid pressure. The Lennard Jones wall models allow the liquid phase to move into the gaseous region with even higher rate than in the diffuse case. This is due to the wall attraction that maintains a liquid film on the boundaries in detriment of decreasing the center channel density. Thus additional wall models are being investigated.
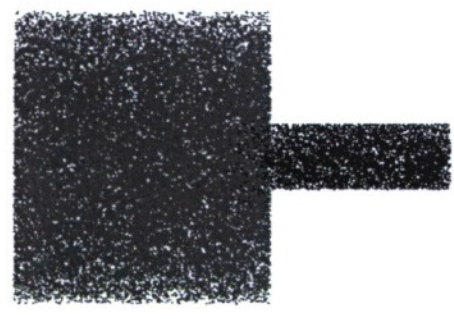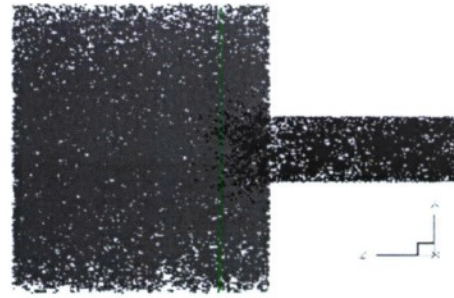
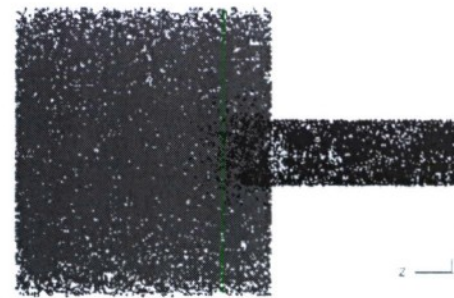Atomistic wall Model
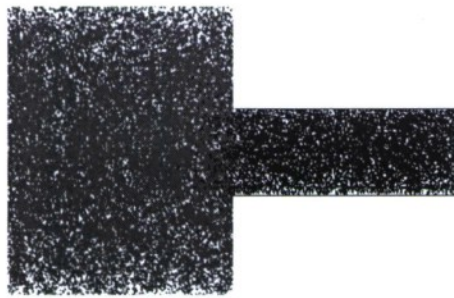
Diffuse wall Model
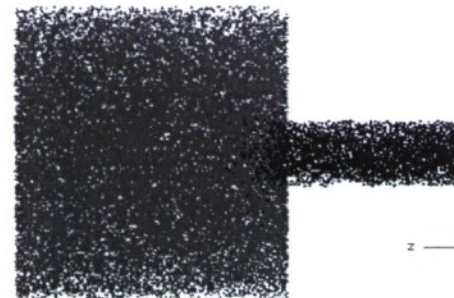
Diffuse + Morse attraction wall Model

Lennard Jones 10-4 wall Model

Lennard Jones 9-3 wall Model
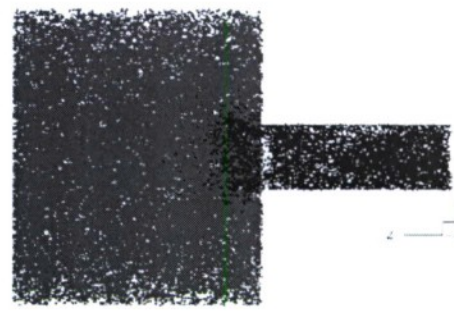
Lennard Jones 6-3 wall Model

Fig. 7   Wall model effects on liquid/gas coexistence.

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Personnel Supported:

        Faculty: Michael M. Micci

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        Undergraduate Students: Michael Barrucco

Publications:

"Comparison of Wall Models for the Molecular Dynamics Simulation of Microflows," R. D. Branam and M. M. Micci. Accepted for publication in Nanoscale and Microscale Thermophysical Engineering, Oct. 2006.

"Molecular Dynamics Simulation of Wall Model Effect on Liquid Nanojet Injection," M. M. Micci and N. Sellami. Submitted to Microfluidics and Nanofluidics, Nov. 2006.

Interactions:

"Large Scale Simulations of Colloid Thrusters – Coarse-Graining Strategies," J. Daily and M. Micci, AIAA Paper 2007-5256, presented at the 43rd AIAA/ASME/SAE/ASEE Joint Propulsion Conference, Cincinnati, OH, July 8-11, 2007.

Michael M. Micci spent the 2006-2007 academic year as a Visiting Professor at the University of London, Queen Mary, United Kingdom, developing a molecular dynamics simulation of electrosprayed ionic liquids in conjunction with Professor John Stark.